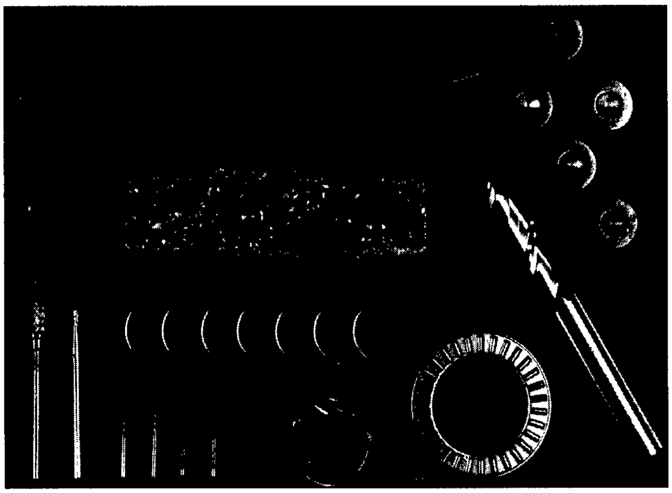
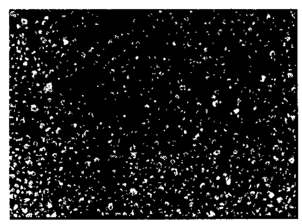
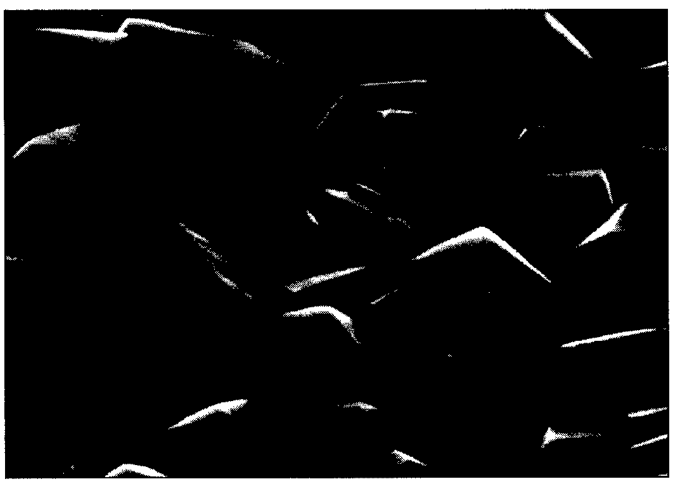
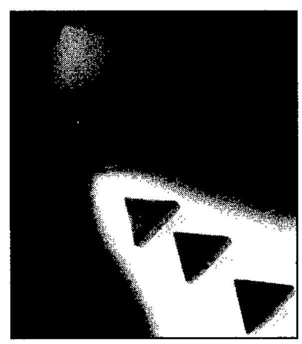
BALLISTIC MISSILE DEFENSE ORGANIZATION



Diamond Technology Initiative







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Diamond Technology Initiative

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BMDO Diamond Technology Initiative
c/o National Technology Transfer Center
Washington Operations
2121 Eisenhower Ave., Suite 400
Alexandria, VA 22314
(703) 518-8800, ext. 500
(703) 518-8986 (Fax)

BALLISTIC MISSILE DEFENSE ORGANIZATION

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Foreword

In 1986, the Ballistic Missile Defense Organization (BMDO) Innovative Science and Technology (IS&T) program began one of its most ambitious projects: the Diamond Technology Initiative. This program's goal is to bring the promise of diamond coating technology to missile defense uses, particularly those made possible by wide bandgap diamond microelectronics. In the process, BMDO has also encouraged commercial use of diamond coating technology. The intent of this report is to help industry take advantage of some of the existing developments in diamond coatings and to foster collaborations that will make future diamond-coated products possible.

Already, the BMDO Diamond Technology Initiative has helped bring three products to the marketplace, nurture three start-up companies that recently completed initial public offerings of stock, foster 22 collaborative ventures designed to introduce future products, and generate at least 51 patent applications (31 of which have been granted to date)—and the payoffs are just beginning. Most of the commercial progress has occurred in small-volume markets like x-ray windows, custom coatings, and certain machine-tool applications. Other, larger markets, such as flat-panel displays that use diamond cold cathodes and microelectronic heat spreaders, are just now emerging.

The big payoff—the one that the BMDO Diamond Technology Initiative set its sights on from the beginning—will not come until diamond semiconductors can be produced with cost/performance benefits that exceed those of devices made from other materials. While that day has not yet come, the BMDO Diamond Technology Initiative continues a broad-based research program in diamond thin-film coatings to produce large-area, single-crystal diamond coatings at a cost competitive with other electronics-grade materials.

Some promising research results have brought BMDO closer to the goal of diamond-thin film semiconductors, although the elusive breakthrough that will allow researchers to grow electronics-grade diamond films on a non-diamond substrate has not yet occurred (or, as this breakthrough is known in the field, large-area, single-crystal heteroepitaxial growth). To explain where that breakthrough might occur, or to find promising diamond coating technologies that are closer to the marketplace, this report contains a brief overview of current diamond research, as well as 25 short descriptions of ongoing and recently completed work by participants in the BMDO Diamond Technology Initiative.

Because many of these 25 participants have conducted research in several different areas, the report is arranged by organization name, not research area. The report, however, does contain an index to help you find information about a specific technical area of interest. In addition, the introduction contains a survey of some concepts related to the production of diamond thin films that will be used throughout the report.

To aid further research on the work mentioned here, each summary also lists points-of-contact, publications of interest, and relevant patents, when possible. If you have trouble reaching any of these contacts, or if you have a general question about diamond technology (technical or business-related), a staff of technology transfer specialists is available to help you. Simply call, write, or fax your request to:

BMDO Office of Technology Applications
c/o National Technology Transfer Center
Washington Operations
2121 Eisenhower Ave., Suite 400
Alexandria, VA 22314
Phone: (703) 518-8800, ext. 500
Fax: (703) 518-8986

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Introduction

Survey of Diamond Thin Film Research

This section provides a short introduction to some important concepts related to applications and production of diamond coatings. The first part highlights the properties and applications of diamond, while the second part describes issues related to the production of diamond films.

Part A: Diamond Properties and Applications

With an extraordinary range of properties, diamond coatings could be used in many areas, from optical coatings to electrical heat spreaders. The following list highlights some of the properties and the resulting uses:

<u>Hardness:</u> Diamond has a hardness of 10,000 kg/mm^2, two times harder than its nearest natural competitor, boron carbide. This hardness makes diamond an excellent coating for machine cutting tools or other areas where wear protection is important.

<u>Coefficient of Friction:</u> With a coefficient of friction of 0.05 to 0.1, diamond equals or betters Teflon®'s "slipperiness." Diamond's low coefficient of friction combines with its hardness to provide an excellent set of tribiological properties (properties related to the interaction between a material's surface and that of other materials). Diamond's tribiological properties make it an ideal coating for bearings, rotating seals, extruders, dies, and cookware.

<u>Tensile Strength:</u> Diamond can withstand stretching forces of 290 kg/mm^2, nearly ten times better than alumina. This strength makes diamond a good candidate for reinforced composites.

<u>Chemical Inertness and Radiation Resistance:</u> Diamond is inert to most corrosive chemicals and is very stable in high-radiation environments. These properties combine with diamond's electrical and wear resistant characteristics to make it attractive in biomedical implants, chemical and petroleum processing and exploration, and electrical devices and sensors for satellites and medical instruments.

<u>Electrical Resistivity:</u> Diamond, with a resistivity of 1×10^{16} ohms per cm, insulates against electricity ten times better than alumina. This resistivity, combined with its high thermal conductivity, makes diamond an ideal heat spreader for microelectronic devices and also for dielectric applications such as high-power, thin-film diamond capacitors.

<u>Thermal Conductivity:</u> For every degree Kelvin, diamond can conduct 2000 Watts of heat per meter, nearly five times more than its next closest competitor, silver. This makes diamond substrates ideal for a wide range of thermal management applications, such as the electronic heat spreader.

Thermal Shock: Diamond can withstand thermal stresses of 10 million Watts per meter, 1,000 times better than Zerodur®. This property is also important for many thermal management applications.

Optical Transmission: Diamond can transmit light with wavelengths from 0.22 to over 100 micrometers, compared to 0.2 to 4 micrometers for silica. This transmission range, combined with a hardness that will prevent damage to the optic, makes diamond an ideal optical coating. Applications abound in x-ray instruments, x-ray lithography membranes, infrared sensors and windows, and microwave tube windows.

Part B: Production of Diamond Thin Films

Growth Processes: Since the late 1970's, when a group of Russian researchers developed the ability to produce high-quality diamond coatings through chemical vapor deposition (CVD), researchers have developed more than 10 different methods for growing high-quality diamond and diamond-like coatings, a list that will certainly grow in the future. Most of these methods are some variant of the original CVD technique. In diamond CVD, researchers mix hydrocarbon gas and atomic hydrogen in a high-temperature, low-pressure reaction chamber and energize it, both by heating the reaction chamber to well over 1000°C and aiming some form of directed energy at the substrate surface. This form of directed energy is what differentiates most CVD processes. For instance, filament-assisted CVD places a wire heat element at the substrate, while plasma-enhanced CVD energizes a plasma local to the substrate surface. Other CVD processes include microwave-assisted CVD, laser-assisted CVD, and various combinations of these, such as microwave plasma-enhanced CVD.

Another method that has received considerable attention is the oxy-acetylene torch method, also known as combustion growth. In this case, combustion of oxygen and acetylene produces a mixture of carbon monoxide, carbon dioxide, hydrocarbon radicals, and hydrogen in the hottest part of the flame; if this part of the flame impinges on a water-cooled substrate, these ingredients mix as they do in CVD processes to produce a diamond film. Because this occurs at room conditions (atmospheric pressure, no special clean-room requirements) and produces diamond at much higher growth rates than traditional CVD techniques, it has extremely low capital and production costs. However, the method has yet to supplant traditional CVD processes because it's difficult to control the quality of the film. Impurities in the oxy-acetylene tank are common, and the growth conditions are more difficult to control than in a traditional CVD reaction chamber.

In laser ablation, another growth technique, a pulsed laser heats a carbon source, thereby producing an energized vapor of carbon atoms that settle on a substrate in a diamond form. Different laser ablation processes have produced several forms of diamond at substrate temperatures significantly lower than in CVD (35°C versus 1000°C). The lower substrate temperature allows researchers to deposit diamond on a wider variety of surfaces since the substrate is less likely to crack during deposition or cooling. Like combustion growth, the

process does not provide as precise control of the deposition process as CVD does. Also, laser ablation rarely produces pure diamond, but rather some form of diamond-like carbon (diamond crystals mixed with impurities such as hydrogen or graphite).

On the other end of the spectrum, some physical vapor deposition techniques—such as atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), and ion implantation—are under development that have much slower growth rates than CVD, but provide extremely fine control over the surface reactions. These methods have such precise control because growth does not occur through a large-scale chemical reaction as in CVD, but by localized reactions that limit growth to as little as one atomic layer at a time.

<u>Growth Theory:</u> Synthetic diamond growth is possible because it is a metastable form of carbon with respect to graphite. That is, it requires less energy to form graphite bonds than diamond bonds; however, if you can exceed the energy barrier between graphite and diamond, you can produce a stable diamond crystal. As a result, all diamond growth processes occur as a competition between graphite and diamond, and any number of factors may cause graphite to win the battle, such as substrate composition, temperature, pressure, or the mix of gaseous precursors.

Another important idea is that there are two steps in the formation of diamond. First, the gaseous reactants must form seed crystals on the deposition surface—a process known as nucleation. Then, a diamond film must grow on these seed crystals. The process of nucleation is poorly understood; all that is really known is that the more the substrate looks like diamond, the more likely it is that hydrocarbon radicals will nucleate in a diamond form. In contrast, growth processes are much better understood, and occur when a hydrocarbon radical bonds with an open site on the surface of a seed crystal. This surface radical can then either:

- Turn back into seed crystal by reacting with a free hydrogen atom or some other atomic species
- Add carbon gas species (probably a methyl radical) to grow diamond
- Decompose into graphite.

Several growth chemistries have been investigated to prevent the seed crystal from decomposing into graphite. The most common techniques use atomic hydrogen. Other atomic species that could maintain or recover the diamond lattice structure by bonding to surface termination sites include oxygen, fluorine, chlorine, and silicon. In addition, many different hydrocarbon reaction sequences have been investigated as possible scenarios for diamond growth.

<u>Production of Electronics-Grade Diamond Coatings:</u> While researchers can grow polycrystalline coatings on any number of substrates, most of the high-payoff applications in

diamond electronics require single-crystal coatings. While many researchers have grown single-crystal diamond coatings, they have only been successful on natural diamond substrates (a process known as homoepitaxial growth). Unfortunately, homoepitaxial growth is too expensive and, because large-area diamond substrates do not exist in nature, cannot occur over a large enough area to make diamond microelectronics cost-competitive with today's devices, even in highly specialized applications.

The only way to make large-area, single-crystal diamond coatings cost-competitive is to grow them on a substrate other than diamond (a process known as heteroepitaxial growth). Unfortunately, lattice mismatches between diamond and non-diamond substrates create epitaxial stresses that cause the diamond coating to crack or decompose into graphite. Lattice mismatches are also a major problem in many other diamond coating applications, such as machine tool coatings and optical coatings, where lattice stresses create poor adhesion between the diamond coating and, say, a tungsten carbide tool bit.

Several techniques are now under investigation to overcome this hurdle, listed as follows:

- **Substrate preparation.** One way to encourage heteroepitaxial growth is to make a non-diamond substrate look more like diamond. By doing so, researchers can increase the number of sites where nucleation occurs, also known as the nucleation density. A non-diamond substrate can be made to look more like diamond by scratching the substrate with a diamond powder or etching diamond-shaped pits into the substrate. Another possibility is to make large-area, diamond substrates out of less expensive, smaller diamond crystals (either natural or synthetically growth through a high-temperature, high-pressure process). Several techniques are now being developed to bond these pieces together, all with the same crystallographic orientation, in a large mosaic.

- **New growth techniques.** One problem with CVD growth processes is that they tend to be uneven. That is, nucleation will occur at one site and diamond will grow on top of the site. Meanwhile, growth does not occur a few microns over because no diamond has nucleated there. As a result, polycrystalline growth occurs instead of single-crystal growth. To prevent this uneven growth, self-limiting growth techniques such as ALE only allow growth one atom-thick layer at a time.

- **Interlayers.** Lattice stresses between diamond and non-diamond substrates such as copper and silicon can be reduced by growing layers of another material between the substrate and the diamond. Silicon carbide and cubic boron nitride are among the interlayers that have been investigated for silicon substrates, while molybdenum has been investigated for copper substrates.

Another problem related to diamond microelectronics involves doping: It is extremely difficult to add the impurities needed to make diamond a semiconductor without destroying its crystalline structure. While several groups of researchers have had success doping diamond with boron and carbon to make a p-type semiconductor, no one has been able to reliably add

n-type dopants. In addition to these difficulties with doping, researchers have had some trouble forming electrical contacts that meet key technical parameters for diamond electronics, such as high-temperature survivability (greater than 500° C), strong adhesion, low contact resistance, and precise dimensional control. These problems, though, do not seem to be as troublesome as those associated with doping.

Miscellaneous Issues: Some other important issues related to diamond thin film research include characterization techniques, post-growth processing, and the development of other materials with properties similar to diamond.

- **Characterization.** Characterization techniques are essential to further advance the ability of researchers to grow high-quality diamond. The two most common characterization techniques are Raman spectroscopy and x-ray diffraction; however, many other characterization techniques have recently been developed that provide new information about diamond coatings. Perhaps the most notable of these are several *in situ* characterization techniques that allow researchers to monitor growth processes as they happen, thereby providing new information about the chemical reactions that occur during growth.

- **Post-growth processing.** As the hardest known material, it is extremely difficult to cut or polish diamond films once they have been produced. This is particularly important in optical applications, where an unpolished surface has a dramatic impact on the reflectivity and refractivity of the finished optic.

- **Other materials.** Researchers can now grow several material coatings with properties that nearly match those of diamond. In many cases, these materials are easier to work with than diamond, making them an excellent alternative to diamond. Diamond-like coatings, discussed earlier in conjunction with the laser ablation growth processes, often nearly match diamond in such properties as hardness, slipperiness, and optical transmission. These coatings often bond more readily with certain substrates, thereby reducing adhesion concerns. Similarly, cubic boron nitride is the second hardest known material and, unlike diamond, will not dissolve in ferrous metals. In addition, some theoretical models have shown that carbon nitride, when bonded in a C_3N_4 configuration, could be harder than diamond. However, no one has yet been able to produce C_3N_4 in the laboratory, and some researchers question whether it is possible for C_3N_4 to exist at all.

Advanced Technology Materials, Inc.

Description: Advanced Technology Materials, Inc., or ATMI (Danbury, CT), is both developing diamond-coating technology for electronics applications and, as the result of other research, manufacturing and selling equipment and materials used in CVD processes. ATMI has received substantial support from the BMDO Small Business Innovation Research (SBIR) program in these two areas.

For example, ATMI recently received a $1 million BMDO SBIR cost-shared contract to develop a prototype field emission display (FED) that uses diamond cold cathodes. Due to diamond's unique electronic properties, diamond cold cathodes can emit electrons while consuming much less power than other materials. As a result, diamond cold cathodes can be used to make FEDs that combine the brightness of active matrix liquid crystal displays with the ease-of-manufacture of current FEDs. By increasing the brightness of FEDs, diamond cold cathodes could pave the way for low-cost production of large-area flat-panel displays. The market for such devices is currently estimated to total nearly $6 billion.

In the process of this work, ATMI has developed broad capabilities in thin-film diamond CVD, doping of diamond to convert it into a semiconductor, and electrical contacting technology—the three components needed to produce working electronic devices. While ATMI's focus is currently on introducing diamond cathode-based FED's to the marketplace, the company also hopes to leverage their technical expertise in diamond electronics to exploit new applications as the technology matures.

Opportunities for Collaboration: ATMI introduced CVD equipment peripherals in 1987 and CVD source materials in 1989. While these products are marketed primarily for traditional semiconductor production (silicon and III-V), many of these products, such as gas purifiers and delivery systems, are also applicable to diamond CVD.

In the area of diamond electronics, ATMI is collaborating with Silicon Video Corporation and the Massachusetts Institute of Technology's Lincoln Laboratory (see page 20) to develop flat-panel displays using diamond cold cathode technology. ATMI—with support from MIT Lincoln Laboratory—will develop the diamond cathodes, while Silicon Video will integrate the final flat-panel display. In addition to these ventures, ATMI recently held an initial public offering of stock to raise the capital needed to introduce new products to the marketplace.

Contact:
Dr. Duncan Brown
Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810
Phone: (203) 794-1100
Fax: (203) 792-8040

Aerodyne Research, Inc.

Description: In a BMDO SBIR project, Aerodyne Research, Inc. (Billerica, MA) is developing an ALE scheme to deposit diamond thin films using halogenated reagents (such as chlorine and fluorine). Because it can provide better-controlled growth than CVD techniques, this scheme is a promising avenue to large-scale heteroepitaxy.

Self-limiting chemical reactions between the diamond coating and halogens provide better-controlled growth of diamond films. Aerodyne has conducted a series of studies on these self-limiting chemical reactions, the most important of which may involve the role of fluorine atoms. Like hydrogen atoms, fluorine atoms help maintain the diamond structure by bonding to surface termination sites of the diamond lattice. Fluorine, though, is not as easily removed from these sites as hydrogen; therefore, fluorinated surfaces offer a better way to control the rate at which reactive sites are formed. Other studies involve the role of chlorine atoms and several molecular species, such as water, oxygen, and alkyl halides.

In an earlier BMDO SBIR project, Aerodyne investigated the tribiological properties of fluorinated diamond thin films. While diamond thin films generally have a low coefficient of friction, their coefficient of friction becomes high when adsorbed water or oxygen is present. Aerodyne investigated fluorination of diamond to reduce the coefficient of friction under these circumstances.

Opportunities for Collaboration: Aerodyne hopes that this research will lead to the first low-pressure, MBE technique to grow diamond, a breakthrough that would have far-reaching impact in diamond electronics. In the meantime, the opportunity for collaboration is limited to information transfer. Aerodyne's work in fluorinated thin films for tribiological applications has greater commercial potential. The company has already worked with several companies on the technique and is willing to consider other collaborations in the future.

Contact:
Dr. Andrew Freedman
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821
Phone: (508) 663-9500 ext. 296
Fax: (508) 663-4918

Publications:
Freedman, Andrew. "Halogenation of Diamond (100) and (111) Surfaces By Atomic Beams," *Journal of Applied Physics*, Vol. 75, No. 6, page 3112, 3/15/94.

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Applied Sciences, Inc.

Description: With the help of BMDO SBIR contracts, Applied Sciences, Inc. (Cedarville, OH) has developed broad expertise in depositing high-quality CVD diamond coatings on many different substrates. One of the company's most noticeable achievements has been its work in the area of polycrystalline diamond fibers (PDF), which are used make diamond-reinforced composites that conduct heat away from electronics.

Applied Sciences makes their PDFs by pre-treating a vapor-grown carbon fiber in an ultrasonic bath of diamond dust in an aqueous solution. The fibers are then placed in a microwave plasma-enhanced CVD reactor, where polycrystalline diamond grows on the carbon fiber. Both the diameter of the precursor carbon fiber and the thickness of the diamond coating can be varied, which allows Applied Sciences to tailor the physical properties of the PDF to meet a specific need.

With Applied Sciences' PDFs providing reinforcement, diamond-reinforced composites can have a thermal conductivity higher than 1000 Watts per meter and degree Kelvin (W/m-K). Also, unlike pure diamond, they can have a coefficient of thermal expansion that matches silicon, gallium arsenide, or any other semiconductor. These two qualities, combined with diamond's high electrical resistivity, make these composites an attractive heat spreader in electronic devices. Others have tried to produce similar composites using diamond particles, but the thermal conductivities of these composites are not much higher than the matrix material. With particles, multiple grain boundaries between the diamond and the matrix materials reduce the composite's thermal conductivity.

The company also has expertise in doping diamond films to make semiconductors and producing diamond-coated insulators for thermionic fuel cells.

Opportunities for Collaboration: Applied Sciences has applied for a patent covering its diamond fiber technology. The company hopes to market the diamond fibers, either as a final composite or as a raw material, to electronics packaging houses, which will use the material to make substrate boards. In the meantime, Applied Sciences is refining their diamond fiber technology so that they can scale it to larger, more economical production volumes. Teaming arrangements may be a possible avenue to reach this stage.

Contacts:
Mr. Max Lake or Dr. Jyh-Ming Ting
Applied Sciences, Inc.
141 West Xenia Ave.
P.O. Box 579
Cedarville, OH 45314-0579
Phone: (513) 766-2020
Fax: (513) 766-5886

Publications:

Ting, J.; Lake, M; and Phillips, J.F. "Diamond Fibers for Thermal Energy Management," *Surface and Coatings Technology*, Volume 62, 1993.

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Crystallume, Inc.

Description: With expertise in all key CVD technologies and the ability to tailor diamond coatings for many applications, Crystallume has become a leader in diamond fabrication technology. As a participant in the BMDO Diamond Technology Initiative, Crystallume (Santa Clara, CA) has won eight BMDO SBIR awards related to diamond CVD technology, four of which won Phase II awards and are described below:

- **PE-CVD Diamond Thin-Films for Tribiological and Optical Materials.** In Crystallume's first BMDO SBIR project, the company developed a predictive growth model for depositing optical- and tribiological-quality diamond thin films on different substrates using plasma-enhanced chemical vapor deposition (PE-CVD).

- **CVD Diamond Packaging for High-Temperature Electronics.** Crystallume also received BMDO SBIR funding to develop a diamond heat spreader to remove heat from microelectronic circuitry. Given that diamond conducts heat better than any other material, diamond heat spreaders would allow electronic devices to be more compactly packaged, to run at higher frequencies and higher temperatures, and to handle higher power loads. The technology is especially attractive for high-power laser diodes, where diamond's low coefficient of thermal expansion allows the package to maintain the close tolerances needed in the connection of the laser diode to a fiber optic wire.

- **Diamond Junction Field-Effect Transistor.** In this project, Crystallume fabricated transistors by depositing heavily doped diamond layers on cubic boron nitride and natural diamond substrates. Diamond transistors offer significant advantages in applications where high-temperature, radiation-resistant, or high-power devices are needed.

- **Low-Friction Diamond Films for High-Payoff Ceramic Bearings.** In this project, Crystallume investigated techniques to deposit diamond thin-films on ceramic bearings. The company has successfully coated spherical ceramic bearings, sized from 1 millimeter to 1 inch in diameter, in collaboration with a bearing supplier and end-user. Diamond coatings significantly enhance ceramic bearings by providing an ultra-hard, low-friction, chemically resistant surface for high-performance military and commercial applications. Uses for diamond-coated ceramic bearings include high-performance aircraft, gyro bearings, precision instruments, and oil and gas downhole drilling and processing equipment.

In the other four projects, Crystallume investigated ways to diamond-coat thermionic insulators, ultraviolet imaging sensors, moderators for nuclear fuel pellets, and gallium arsenide substrates.

Opportunities for Collaboration: Crystallume currently markets three diamond-coated products. They are:

- **Microelectronic Heat Spreaders.** This heat spreader uses diamond's high thermal conductivity to remove heat from electronic devices. The primary applications to date for these heat spreaders are in laser diodes used in fiber optic communications systems and high-power laser diode arrays for military, communications, and scientific instrumentation.

- **Diamond-Coated Tungsten Carbide (DCC™) Cutting Tools.** Crystallume initially developed these tools under a contract from the National Center for Manufacturing Sciences (NCMS). This collaboration incorporated major cutting tool suppliers and end users, including General Motors, Ford Motor, Teledyne, Valentine, and others. In this project, Crystallume solved the adhesion problems traditionally associated with CVD diamond deposition on the cemented carbides used in cutting tools. The company is now selling DCC™ inserts for field qualification and will be providing cutting tools in quantity by the end of 1994. The diamond-coated cutting tool business is estimated at $450 million worldwide by the year 2000.

- **Ultra-Thin X-Ray Window.** Introduced in 1989, the x-ray window was the first commercial product in the world using a diamond CVD coating. This window is less than 0.5 microns thick and supports a one-atmosphere pressure differential, thereby eliminating the complex turret mechanisms previously used in low-energy elemental analysis. These windows are currently used in energy dispersive x-ray detectors, x-ray spectrometers, and other x-ray instruments.

The company is also involved in a number of development projects, including one associated with the Diamond Tool Consortium and another in the form of a cooperative research and development agreement (CRADA) with Los Alamos National Laboratory.

The Diamond Tool Consortium—with members such as General Motors, Hughes Aircraft, and Boeing Commercial Aircraft—recently won a $3.5 million Advanced Technology Program award from the National Institute of Standards and Technology. In this project, the consortium will extend Crystallume's proprietary technology for diamond-coating tungsten carbide cutting tool inserts to the more difficult problem of coating rotating tools such as drills, reamers, and end mills for machining advanced composite materials.

In the Los Alamos CRADA, Crystallume will develop diamond-based sensors that measure the intensity and distribution of radiation. These sensors will permit better measurement and control than existing silicon devices in applications such as radiation therapy, nuclear and particle physics research, atomic power generation, and environmental radiation monitoring.

In addition, on March 16, 1994 Crystallume completed an initial public offering of 1 million common shares of stock and 1 million redeemable warrants. Through this stock offering, Crystallume raised over $5 million for the commercialization of its diamond-coated products.

Crystallume has 19 patents for diamond CVD technology (17 U.S.), a number of which were the direct result of the BMDO SBIR projects mentioned above.

Contact:
Ms. Laurie Conner
Vice President of Marketing and Sales
Crystallume
3506 Bassett Street
Santa Clara, CA 95054
Phone: (408) 653-1700 or (800) 789-4DCC
Fax: (408) 653-1710

Publications:

1994

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Mumm, D.R. et al., "High Temperature Hardness of Chemically Vapor-Deposited Diamond," *Journal of the American Ceramic Society,* 76 [1] (January 1993) pp. 238-240.

For a full list of publications—including those published between 1987 and 1992—call Laurie Conner at the above phone number.

Emcore Corporation

Description: Emcore Corporation (Somerset, NJ) recently completed a Phase I BMDO SBIR contract to investigate an ALE technique for depositing diamond films on silicon. In this project, Emcore used halogenated carbons to provide self-limiting growth, or passivation. In addition, Emcore's technique uses supersonic beams to accelerate the reactants, thereby adding to the activation energy needed to make them react with the heated substrate. This combination of halogen passivation and kinetic activation may provide better controlled growth, and is therefore a promising route to single-crystal heteroepitaxy.

Opportunities for Collaboration: Emcore is continuing to develop this process for the growth of silicon carbide, which has a more immediate market potential. Because diamond growth on silicon probably requires a silicon carbide interlayer to reduce strain defects, this work may lead to advances in diamond growth through ALE.

Contact:
Dr. Heng Liu
35 Elizabeth Ave.
Somerset, NJ 08873
Phone: (908) 271-9090
Fax: (908) 271-9686

Epion Corporation

Description: Epion Corporation (Bedford, MA) has received three BMDO SBIR contracts related to diamond thin-film technology, one that is still ongoing and two that have been completed. During these contracts, which are described in more detail below, Epion has developed expertise in filament-assisted CVD, selective nucleation of diamond, fabrication of diamond membrane structures, and ion beam processes for the nucleation of diamond.

Thin Diamond Lenses

In a completed project, Epion developed a method to produce shaped diamond membranes to be used as lenses. To produce thin diamond lenses, Epion deposits a diamond film onto a silicon disk substrate that has been machined to have a contour that complements the curved lens. After deposition, the exposed surface of the diamond must be polished flat and smooth. Then, the center area of the silicon substrate can be removed by chemical etching, thereby leaving the shaped diamond membrane lens supported by a silicon ring. Adequate polishing of one face of the diamond was a difficult problem not solved during this effort.

CVD diamond for optical applications should have a void-free microstructure and good optical transparency. To achieve these goals, Epion initially developed a selective nucleation method for producing films with a highly uniform grain structure. A focused ion beam was used to mill patterns of very small, precisely spaced receptacles into polished silicon substrates. During subsequent filament-assisted CVD growth, diamond would nucleate only at the seed crater sites. The resulting diamond films had dense patterned microstructures and suitable optical characteristics. Epion also found that they could produce acceptable optical diamond without selective growth by increasing the nucleation density to very high levels.

Single-Crystal Heteroepitaxy

Materials such as copper, with lattice structures similar to diamond's, are good candidates for producing single-crystal diamond films on a non-diamond substrate. As a result, Epion has been investigating ion implantation of carbon into copper at high temperatures, a variation on an approach proposed earlier by Johan Prins of the University of Witwatersrand, South Africa. Epion has expertise in producing single-crystal copper films on silicon. The company believes this expertise could be extended to the heteroepitaxial nucleation of diamond on copper, thereby leading to large-area single-crystal diamond films. While Epion has not yet found a heteroepitaxial nucleation process for copper, the company is extending their specialized ion implantation capabilities to other candidate substrate materials.

Diamond Insulator for Silicon-on-Insulator Microelectronics

In another project, which produced a successful proof-of-principal but was tabled due to a lack of funding, Epion worked to develop diamond coatings for silicon-on-insulator (SOI) microelectronics. SOI materials use an electrical insulator to isolate a thin silicon semiconductor layer from its substrate. This isolation allows SOI devices to run faster, better

withstand radiation, and operate at higher temperatures than devices fabricated using standard silicon wafers. With a much higher thermal conductivity and electrical resistivity than silicon dioxide, diamond is an attractive alternative to the silicon dioxide insulators used in conventional SOI devices. In this project, Epion showed that they can produce silicon-on-diamond SOI structures in a two step process. First, they deposit diamond onto the device-layer silicon of a commercially available SOI wafer. Then, they chemically remove the wafer base using the original insulating layer as an etch stop.

Opportunities for Collaboration:
Epion is working with a supplier of custom optical components to begin marketing diamond optical components. These components are intended for applications in the far infrared region of the spectrum, where highly polished surfaces will not be required. Epion hopes introduction of these products will pave the way for higher volume applications.

Epion will consider collaborating with interested parties in a wide range of diamond coating applications. They are currently collaborating with other organizations on two projects. The first project is develop fuel cell electrodes with electrically conductive diamond coatings, while the second project is to develop diamond coatings for medical implants.

Epion holds one patent related to a technique for selective nucleation of diamond.

Contact:
Mr. Allen Kirkpatrick, President
Epion Corporation
4R Alfred Circle
Bedford, MA 01730
Phone: (617) 275-3703
Fax: (617) 275-3709

Iowa Laser Technology, Inc.

Description: In June 1992, Iowa Laser Technology, Inc. (Cedar Falls, IA) completed a BMDO SBIR contract to develop a new diamond thin film deposition technique using a laser as the source of energy and a carbon source such as soot. Such a system could offer low-temperature deposition along with high growth rates.

During this research, Iowa Laser attempted to deposit diamond under various growth conditions. Generally, these conditions included a gas-filled chamber at atmospheric pressure, using either a CO_2 or YAG laser. In addition to soot, Iowa Laser used carbon monoxide, carbon dioxide, and graphite as carbon sources. The company also attempted deposition on several different substrates, including silicon, copper, and graphite.

While Iowa Laser was not able to reliably deposit diamond using this method before termination of the contract, several samples showed evidence of diamond growth when examined with a scanning electron microscope.

Opportunities for Collaboration: Although work has discontinued on the project due to a lack of funding, Iowa Laser has a patent for the deposition process and will consider working with interested parties—either through licensing or joint development—on a case-by-case basis.

Contact:
Mark Baldwin
Iowa Laser Technology, Inc.
6122 Nordic Drive
Cedar Falls, IA 50613
Phone: (319) 266-3561

Linares Management Associates, Inc.

Description: Linares Management Associates, Inc., or LMA, Inc. (Medfield, MA) was formed to develop and manufacture new wide bandgap semiconductor materials for device fabrication. The company has BMDO SBIR funding to develop free-standing single-crystal plates of diamond and gallium nitride (GaN). These two materials will be used as substrates for the homoepitaxial growth of diamond or GaN films and subsequent fabrication of active semiconductor devices. The use of single-crystal substrates of diamond is expected to result in diamond films with superior electrical properties compared to polycrystalline or heteroepitaxial diamond films. Similar improvement in GaN films are expected from the use of GaN substrates.

Of these two material development projects, diamond is currently at a more advanced state simply because of the age and funding of the programs. The company can produce free-standing single-crystal diamond plates up to 7 millimeters in diameter. Using these plates as substrates, the company grows homoepitaxial boron-doped semiconducting diamond films. These substrates and films are large enough to develop advanced devices and the company expects to offer single-crystal diamond substrates on a limited commercial basis in the near future.

Opportunities for Collaboration: While LMA does all of its crystal growth research in its own laboratories, it also has programs with the University of Florida, Department of Materials Science and Engineering and some major companies for specialized measurements, device fabrication, and testing. The company will consider similar partnerships on a case-by-case basis.

In addition, LMA, Inc. plans to be a major supplier of wide bandgap semiconductor substrates and active layers for device development and production. The company is dedicated to the principals of world class manufacturing and to close interaction with customers.

LMA, Inc. has patents pending for its method of producing free-standing, single-crystal diamond plates.

Contact:
Dr. Robert Linares
Linares Management Associates, Inc.
93 West Street
Medfield, MA 02052
Phone and Fax: (508) 359-9680

Lintel Technology, Inc.

Description: Lintel Technology Inc. (Roslyn, NY) has developed a method to bond diamond to a metal substrate, a process useful for producing diamond heat spreaders used in microelectronic devices. While metal-ceramic joints typically cannot withstand rapid thermal cycling, Lintel has developed a method to microengineer the interfacial bonding region using a tungsten/molybdenum fusion-metallizing technique. This technique can produce diamond heat spreaders that strongly bond to metal substrates and resist both thermal and mechanical shock. The method allows bonding at mass production rates, thereby opening applications for diamond heat sinks in defense, automotive, aerospace, and electronics.

Opportunities for Collaboration: While the BMDO SBIR program provided early support of this research in a Phase I feasibility study, Lintel has since continued this research with internal funds and some private sector funding. The company will consider collaborating with other organizations on a case-by-case basis.

Lintel has received several patents on diamond and ceramic bonding, with other patent applications pending on diamond heat sinks and diamond bonding or coating.

Contact:
Dr. Chou H. Li
Lintel Technology, Inc.
379 Elm Drive
Roslyn, NY 11576
Phone: (516) 484-1719
Fax: (516) 484-7136

Publications:
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Massachusetts Institute of Technology Lincoln Laboratory

Description: The BMDO Diamond Technology Initiative is currently supporting diamond electronics research at MIT Lincoln Laboratory (Lexington, MA) to produce diamond electrical devices, to produce a mosaic diamond substrate for single-crystal homoepitaxy, and to develop diamond cold cathodes.

In the first effort, Lincoln Laboratory researchers are investigating methods to improve the rectifying characteristics of mercury-diamond Schottky diodes. They have found that plasma treatments with some gases (N_2 or CF_4 with 8.5 percent O_2) reduce the leakage current in Schottky p-type diamond diodes (other gases, such as N_2O, H_2 or O_2 can increase the leakage current). In addition, the Lincoln Laboratory researchers have developed an annealing process that can substantially increase the forward conductance of the diode.

In the second effort, the researchers have developed a method to produce large-area diamond substrates by orienting smaller diamond cubes in a mosaic pattern. This pattern can very closely approach single-crystal quality, thereby allowing the researchers to grow electronic-grade, single-crystal diamond on the diamond substrate.

To produce this substrate, the researchers distribute a layer of several hundred cubes (obtained commercially through a supplier of high-pressure, high-temperature diamond) on a smooth, non-diamond substrate. When wetted with a mixture of isopropyl alcohol and glycerin, these cubes coalesce into small domains of 20 to 30 cubes (this coalescing occurs as a result of the surface tension of the liquid mixture). The crystals that make up these domains all have the same crystallographic orientation; unfortunately, the process forms many such domains and they are randomly oriented. To obtain uniform orientation, Lincoln Laboratory researchers use one of two techniques: they can either align the domains next to vertical square walls that surround the substrate, or use a metal probe to push on a layer of the domains. By pushing on the structure layer, the domains rotate until they are all oriented in the same way.

Lincoln Laboratory researchers are also investigating diamond cold cathode technology. Diamond is an attractive emitter of electrons because it requires comparably little voltage to pull electrons out the material (about 5 volts versus 10 volts for other devices), does not readily fail like metal tip emitters, and is not easily contaminated like conventional semiconductor emitters. Lincoln Laboratory produces diamond cold cathodes by forming diodes in p-type semiconducting diamond using carbon ion implantation into the diamond substrate. When forward biased, these diodes emit current into the vacuum with an efficiency varying from $2x10^{-4}$ to $1x10^{-10}$.

Opportunities for Collaboration: Under ARPA sponsorship, MIT Lincoln Laboratory is currently collaborating with Advanced Technology Materials, Inc. (ATMI) and Silicon Video, Inc. to produce a flat panel display using diamond cold cathodes. In this project, MIT Lincoln Laboratory is working with ATMI to produce the diamond cold cathodes for the displays, while Silicon Video will produce the final product.

Lincoln Laboratory will also consider forming other collaborations to commercialize its diamond electronics technology. The laboratory has received two patents for diamond electronics technology, which are available for license to interested parties.

Contact:

Dr. Michael Geis
MIT Lincoln Laboratory
Microelectronics Group, Solid State Division
Lexington, MA 02173-0073
Phone: (617) 981-4658
Fax: (617) 981-4983

Publications:

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Morgan State University

Description: To provide information on wide bandgap materials (such as diamond) that may be used for high-power, high-frequency amplifiers, researchers at Morgan State University (Baltimore, MD) are experimentally investigating carrier drift velocities in high-strength electric fields. These measurements employ the transient charge, or time of flight method, in which an electron beam probe measures how long electron collisions last—a key parameter in determining carrier mobility in a semiconductor.

Morgan State researchers have designed and constructed a measurement system that includes a scanning electron microscope with a photocathode electron gun and a femtosecond pulsed laser. This system can characterize narrow drift regions and perform high-field measurements without thermal heating. So far, the Morgan State researchers have performed initial photocurrent measurements on silicon and gallium arsenide semiconductors.

Opportunities for Collaboration: This research is still at an early stage, with opportunities for collaboration primarily limited to information transfer.

Contact:
Craig J. Scott
Department of Electrical Engineering
Morgan State University
5200 Perring Parkway
Baltimore, MD 21239
(410) 398-3298
cjscott@moeng2.morgan.edu

Naval Command, Control, and Ocean Surveillance Center

Description: Researchers at the Naval Command, Control, and Ocean Surveillance Center, or NCCOSC (San Diego, CA), are finding ways to produce working diamond microelectronic devices. As part of this effort, they have developed a method for bonding electrical contacts to diamond. They have also developed an ion implantation technique to dope diamond with boron and carbon, thereby turning it into a p-type semiconductor, and built a working metal-insulator-semiconductor field-effect transistor (MISFET).

The NCCOSC researchers' earliest work centered around bonding electrodes to diamond semiconductors, thereby forming ohmic contacts. Using a patented contact formation technique, the researchers have produced ohmic contacts that meet the key technical parameters of high-temperature survivability (greater than 500° C), strong adhesion, low contact resistance, and precise dimensional control. The NCCOSC team produces these contacts using carbide-forming materials such as molybdenum, titanium, vanadium, and tantalum.

More recently, the NCCOSC researchers have developed a doping technique that uses ion implantation of carbon and boron on natural II(a) diamonds. This work has concentrated both on the effects of temperature on doping and on the order in which carbon and boron are implanted. As a result of this work, the researchers have developed a multi-stage, low-temperature boron implant procedure that is followed by high-temperature (1263 Kelvin) annealing under dry nitrogen. This procedure uses three different implantation energies to produce an 200 nanometer-thick, p-type semiconductor layer with a near uniform concentration of dopants.

These two developments have allowed the NCCOSC researchers to build working MISFET transistors. Using two of these transistors, they have formed a simple circuit with a voltage gain of 2x.

Opportunities for Collaboration: The NCCOSC's patent covering the formation of ohmic contacts is available for license. The researchers will also consider other cooperative arrangements—both formal (such as a cooperative research and development agreement) and informal—on a case-by-case basis.

Contacts:
Dr. James Zeidler
Naval Command, Control, and Ocean Surveillance Center
Code 804
San Diego, CA 92152-5000
Phone: (619) 553-1581
Fax: (619) 553-1718

Dr. Charles Hewett
Naval Command, Control, and Ocean Surveillance Center
Code 561
San Diego, CA 92152-5000
Phone: (619) 553-5301
Fax: (619) 553-1060

Publications:

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Moazed, K.L. et al. "Ohmic Contacts to Semiconducting Diamond," *IEEE Electron Device Letters*, Vol. 9, No. 7, July 1988.

Naval Research Laboratory

Description: The Naval Research Laboratory, or NRL (Washington, DC), recently completed a comprehensive, internally funded (Office of Naval Research and NRL) research program in diamond thin-film coatings, with supplemental funding from BMDO. This effort pursued theoretical and experimental research to develop diamond thin-film growth techniques and devices. As a result of this research, NRL has:

- Developed *in situ* laser diagnostics, which allow researchers to determine the gas phase concentration above a growing film. Detection of these molecular and atomic species has played an important role in modeling the gaseous chemistry and growth mechanisms of CVD processes.

- Determined the structure, composition, and reactivity of the diamond surface during growth. This information has allowed researchers to better control surface growth.

- Calculated a many-body potential function that mathematically describes hydrocarbon bonding. This function is needed to produce computer simulations of diamond growth and is currently used by 10 institutions in their modeling efforts. In addition, the function is useful for other simulations, such as those used to model fullerene production.

- Calculated the rate of hydrogen sticking and abstraction during diamond growth. This calculation allows researchers to determine the number of open sites that can bond with carbon species when producing a diamond structure. Other important theoretical achievements include determining dopant structures and energetics, and band structures and alignments at interfaces.

- Developed several new deposition techniques, most notably combustion growth, in which a flame from an oxy-acetylene torch is used to deposit diamond on a substrate.

- Developed a method to coat fibers with diamond.

- Deposited a diamond coating on aluminum at a low substrate temperature.

NRL is continuing diamond research with funding from the Office of Naval Research, the Advanced Research Projects Agency, and the National Aeronautics and Space Administration. In addition, one group of NRL researchers is continuing to receive BMDO funding to conduct theoretical studies of diamond film growth and its properties.

Opportunities for Collaboration: With expertise in theoretical modeling, characterization, deposition techniques, process control, and experimental surface chemistry studies, NRL has much to offer industry through a cooperative research and development agreement (CRADA) or other arrangement. In addition, NRL has patented, or is in the process of patenting over 17 diamond-related technologies, all of which are available for license.

Contacts:

Overall program:
Dr. James Butler
Naval Research Laboratory
Gas/Surface Dynamics Section, Code 6174
4550 Overlook Ave., S.W.
Washington, DC 20375-5000
(202) 767-1115

Theoretical studies:
Mr. Warren Pickett
Naval Research Laboratory
Complex Systems Theory Branch, Code 4604
4550 Overlook Ave., S.W.
Washington, DC 20375-5000
(202) 404-8631

Publications: NRL researchers have published over 300 papers in refereed journals, proceedings of professional society meetings, and other publications. To receive a list of these publications, please call one of the contacts listed above.

North Carolina State University

Description: Researchers at North Carolina State University's (NCSU) Materials Research Center are studying methods to better characterize the nucleation and growth of diamond, the properties of diamond interfaces, and the nucleation and growth of cubic boron nitride. One of the most important results of this work is the discovery that small-scale heteroepitaxy on silicon is accompanied by a silicon carbide interlayer. This discovery has led to work on both a new nucleation technique for diamond deposition on the silicon carbide layer, known as bias-enhanced nucleation, and the growth of planar surfaces on the diamond films.

<u>Characterization of Diamond Nucleation and Growth</u>
By using several characterization techniques, NCSU researchers have studied the diamond nucleation and growth process, and the effect of process conditions on final diamond film quality. They have supplemented standard diamond characterization techniques such as Raman scattering, scanning electron microscopy, x-ray diffraction, and transmission electron microscopy with several other advanced characterization techniques, such as:

- **Laser Reflection Interferometry (LRI).** LRI, which is an in-situ technique, monitors growth rate by measuring interference patterns that result from the reflection of laser beams off the diamond film. Because these patterns depend on the thickness of the film, they allow researchers to monitor the growth rate in real time. As a result, researchers can vary process parameters during a single deposition and determine the effect of these changes, thereby providing them with more information about the deposition process in a fraction of the time.

- **Photoemission Spectroscopies.** Photoemission spectroscopies provide extremely accurate measurements of diamond surface structures and can do so before the sample is exposed to the atmosphere or is otherwise contaminated. As a result, these techniques are known as in-line characterization. There are many types of photoemission spectroscopy, such as angle-resolved ultraviolet photoemission, Auger electron, x-ray photoemission, and electron energy loss. These techniques are usually used to distinguish between diamond and graphite surface structures.

- **Scanning Tunneling Microscopy (STM).** With atomic-scale resolution, the STM allows researchers to directly visualize the atomic structure of a surface. In addition, the STM can locally measure the electronic properties of a surface. Although the STM can usually only image conducting surfaces (including doped diamond), the NCSU researchers found that they can image thin films of undoped diamond. This capability has allowed them to detect the presence of a silicon carbide interlayer between diamond films and silicon substrates. STM images have also provided evidence of lateral growth (rather than growth in varying directions at different surface sites), which indicates that single-crystal growth is possible on a silicon substrate, at least in principal.

Characterization of Diamond-Metal Interfaces

To make diamond-based transistors, researchers must develop methods to deposit metal contacts on a doped diamond transistor. As a result, the NCSU researchers have studied properties of the diamond-metal interfaces resulting from these contacts. These studies have provided information about the Schottky barrier height of the interface, the electron affinity of the contact surface, and the nature of contacts made of different metals (i.e., whether it is rectifying or ohmic).

In addition to the characterization techniques mentioned above, the NCSU researchers have used luminescence imaging techniques during these studies. Luminescence processes involve the emission of light when excited by a laser beam (photoluminescence) or an electron beam (cathodoluminescence). Due to the nature of the emission, cathodoluminescence is generally best for measuring the electronic properties of the material, while photoluminescence is best for measuring the material structure.

Characterization of Cubic Boron Nitride

NCSU researchers have also begun characterization studies of cubic boron nitride, a ceramic material whose structure and properties are similar to diamond. Early work has centered on the phase evolution of boron nitride (BN) during CVD growth. This work has determined that the BN is first deposited in a thin amorphous structure, then in an layered hexagonal structure, and then finally in a cubic structure.

Bias-Enhanced Nucleation

Rather than enhancing nucleation by treating a substrate with scratches (see page 4, "Substrate Preparation"), this technique uses a negative voltage bias to encourage the methane-hydrogen plasma to react with the substrate. Once diamond growth begins, the bias voltage is removed. By combining this technique with their understanding of the silicon carbide interlayer, the NCSU researchers have begun to develop a technique for enhancing the nucleation of highly-oriented diamond films on a non-diamond substrate. One advantage of the technique is that it is *in-situ*; that is, the substrate can be pre-treated without stopping the reaction or handling the substrate.

Opportunities for Collaboration: NCSU researchers have already worked with a number of other organizations to help them characterize the diamond films they produce, and will consider doing so for other organizations as well. In addition, this research has led to many patentable innovations that are available for licensing from North Carolina State University. These patents include:

- U.S. Patent Applications Serial No. 07/811,425: "Nucleation Enhancer for Chemical Vapor Deposition of Diamond" by Glass et al. Filed 12/20/93.

- U.S. CIP Patent Application Serial No. 07/937,481: "Nucleation Enhancer for Chemical Vapor Deposition of Diamond," by Glass et al. Filed on 8/28/92 (NCSU File# 91-24CIP1). NCSU has responded to the First Official Action by the PTO in November 1993.

- PCT Application No. PCT/US92/11091: "Nucleation Enhancer for Chemical Vapor Deposition of Diamond" by Glass et al. Filed on 12/18/92 (NCSU File) This patent application should enter the national phase within this calendar year.

- U.S. Patent Application Serial No. 08/128,365: "Method for Fabricating Diamond Films and Related Structures," by Glass et al. Filed on 9/28/93 (NCSU File # 94-01).

Contacts:

Dr. Robert F. Davis, Phone: (919) 515-2867
Dr. Robert Nemanich, Phone: (919) 515-3225
Dr. Jeffrey Glass, Phone: (919) 515-2867 or (919) 549-9823
North Carolina State University
Campus Box 7919
Raleigh, NC 27695-7919
Fax: (919) 515-3419

Publications:

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Ohio University

Description: Researchers at Ohio University (Athens, OH) have developed techniques to observe the surface processes of CVD diamond *in situ* and in real time using electron emission microscopy. Two forms of electron emission microscopes have been used—the photoelectron emission microscope (PEEM) and the low energy electron microscope (LEEM)—both of which provide the ability to directly observe changes in the surface of diamond at the relatively high pressures (up to 10^{-3} Torr) and high temperatures (1500 Kelvin) required for CVD diamond growth.

This capability has provided new insights into the growth, nucleation, and material properties of diamond coatings—insights that are of use to both the fundamental and applied research communities. Highlights include:

- **Low-Field Electron Emission.** The emission electron microscope is ideally suited to observe low-field, room-temperature emission of electrons from a CVD diamond film. These low-field cold emitters could be used for high-power, high-frequency vacuum microelectronic devices, such as those used in flat-panel, field-emission displays now under development.

- **Heteroepitaxy.** In using the PEEM to monitor the growth of carbon on molybdenum, the Ohio University researchers have identified a nucleation process that they believe may be a first step toward diamond heteroepitaxy. In this process, the carbon layer nucleates on the molybdenum surface in an ordered pattern that may serve as a precursor to diamond growth.

- **Role of Hydrogen.** The PEEM also allows researchers to observe the effect of atomic hydrogen on the diamond surface, in the form of a characteristic electron emission. Observing this effect may help researchers determine the role of atomic hydrogen in the growth process. LEEM imaging has also provided diffraction patterns that show the surface structures related to hydrogen surface termination.

- **Nucleation and Growth of Diamond on a Molybdenum Surface.** During the growth of sparsely nucleated diamond films on a molybdenum surface, the Ohio University researchers observed the role that carbides play in the nucleation of diamond. In particular, they used the PEEM to observe diamond crystals dissolving into the molybdenum substrate and oxygen etching of diamond.

- **Synchrotron PEEM.** Because synchrotrons provide a much more intense light source than typical laboratory sources, Ohio University researchers have used synchrotron radiation as a light source in PEEM. The added intensity may be used for spectroscopic imaging of diamond surface termination sites.

Opportunities for Collaboration: While most of this research is aimed toward a fundamental understanding of diamond growth and nucleation, the electron emission microscopy studies can provide important insights into other groups' research, particularly in the areas of diamond cold cathodes and heteroepitaxy. The Ohio University researchers will consider collaborations on a case-by-case basis.

Contact:

Dr. Martin Kordesch
Department of Physics and Astronomy
Condensed Matter and Surface Science Program
Ohio University
Athens, OH 45701-2979
Phone: (614) 593-1703
Fax: (614) 593-0433

Publications:

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Penn State University
Department of Materials Science & Engineering

Description: A team of researchers at Penn State University are developing a model to describe how diamond films grow on a surface, and how co-deposited graphite-like materials are etched off the surface or converted to diamond-like carbon. The team is also working on a cyclic CVD process for diamond growth, and have used their diamond growth model to reliably predict trends in growth behavior with experimental parameter changes. At a given growth rate, the cyclic process research is focused on sequentially altering the growth/etching process to produce higher quality films than are typical for non-cyclic growth methods.

Diamond Growth Theories

The Penn State team began developing molecular level theories of diamond growth by modeling surface reactions of adsorbed hydrocarbons on specific surface sites. The team presented early arguments to show that methane (and thus methyl radicals) and acetylene would be the most abundant gaseous species to contact the diamond surface when using methane as the initial hydrocarbon source. They also initially suggested that growth occurred through the incorporation of acetylene into the diamond lattice. However, mechanisms developed later indicated that reaction sequences involving both methyl radicals and acetylene species should be more favorable for growth. They have also examined the role of oxygen in diamond growth.

A mechanism for the co-deposition of graphite-like materials through aromatic hydrocarbon intermediates has also been proposed. The aromatic species can condense on diamond surfaces and act as templates for graphite-like carbon growth. Calculations of kinetic energy showed that molecular hydrogen helps to hinder aromatic formation at the same time that atomic hydrogen is creating active surface sites for diamond growth and helping to etch graphite-like carbon.

Cyclic CVD Diamond Growth Process

This process alternates short periods of diamond growth with short periods where non-diamond deposits are removed, instead of allowing both to occur concurrently at different lattice sites. During the growth phase, the reactant gas typically contains methane (or some other hydrocarbon), while the etchant mixture typically contains oxygen and hydrogen (according to diamond growth theories, atomic oxygen and hydroxyl primarily etch graphite off the growth crystal).

The cyclic method may increase growth rate and film quality by optimizing the growth and etch processes. In non-cyclic CVD processes, a diamond film can grow over and bury the graphite-like carbon before it is etched from the growth surface. With time, these non-diamond deposits may poison growth sites and thus slow the net growth rate, so that even fast growth techniques eventually slow down. By separating etching from growth, the cyclic method may allow the etchant gases to thoroughly remove non-diamond deposits, thereby providing optimal deposition conditions for the growth phase.

Opportunities for Collaboration: In addition to their own experimental research, the Penn State team is collaborating with several other experimental groups—including the Research Triangle Institute—to help explain experimental observations and test their growth models. The research team will consider similar collaborations on a case-by-case basis.

As a result of earlier work on the gas-phase nucleation and growth of diamond powders, the Penn State team has also received one patent for a technique to produce very clean, fine diamond powders (100 to 1000 ångströms thick) using an activated CVD process. Because these diamond powders are much finer and of higher quality than diamond powders produced using high-temperature, high-pressure processes, they may be used in fine polishing processes for precision optics, semiconductors, computer disks, and other devices. This technique (which is covered by U.S. Patent number 5,087,434; February 11, 1992; "Synthesis of Diamond Powder in the Gas Phase") is available for licensing from Penn State University.

Contacts:

Dr. Karl Spear
Professor of Ceramic Science
Department of Materials Science and Engineering
Penn State University
118 Steidle Building
University Park, PA 16802-5005
Phone: (814) 865-0990
Fax: (814) 865-2917
e-mail: kes@psuvm.psu.edu

Dr. Michael Frenklach
Fuel Science Program
Department of Materials Science and Engineering
Penn State University
202 Academic Projects Building
University Park, PA 16802-2303
Phone: (814) 865-4392
Fax: (814) 865-3075
e-mail: iy2@psuvm.psu.edu

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Penn State University
Intercollege Materials Research Laboratory

Description: The Pennsylvania State Intercollege Materials Research Laboratory (IMRL)—the University added the prefix "Intercollege" to its well-known Materials Research Laboratory in 1993—introduced and championed diamond thin-film technology in the United States in 1984. In 1986, the IMRL launched a major program in diamond research, with support from the Office of Naval Research (ONR) for the first year and subsequently from BMDO.

IMRL pursues broad-based research in many areas. As a result, the program has attempted to install nearly every chemical and physical vapor deposition (CVD and PVD) synthesis tool available. To date, the four principal investigators at IMRL have published over 200 papers on CVD diamond and presented even more papers. The program's current research thrusts include:

- Diamond synthesis through a low-pressure solid-state-source (LPSSS) process and other innovative, high-risk approaches

- The development of techniques to deposit thin-film coatings of cubic boron nitride, the principal competitor for diamond in many industrial applications

- The development of electronic applications of diamond based on perfect single-crystal films

- The pursuit of new techniques to grow diamond-like carbon films.

Part of the IMRL effort is the Diamond and Related Materials-Information Consortium (DRM-IC), which evaluates and disseminates information about the status of diamond and related materials research to the corporate world. The DRM-IC evolved from the Diamond and Related Materials Consortium (DRMC), which pursued generic diamond research and provided other pre-competitive services for member companies (which reached 30 at the consortium's peak). The laboratory changed the DRMC's name and shifted its focus in September 1993, in response to the growth of the diamond thin-film industry since 1986.

The BMDO Diamond Technology Initiative has supported many IMRL's activities from the beginning, especially in the use of thin-films for electronics. Industrial members of the DRMC (numbering 45 over a seven-year period) and the State of Pennsylvania's Ben Franklin Partnership Program have also supported IMRL's research activities. Furthermore, federal agencies such as ONR, the Advanced Research Projects Agency, and the National Science Foundation are supporting various aspects of the principal investigators' research.

Opportunities for Collaboration: The Penn State IMRL works with industry by:

- Transferring knowledge and evaluating diamond research through the DRM-IC
- Accepting direct contracts or grants from companies to research specific areas (with appropriate proprietary protection), provided there are no pre-existing conflicts of interest
- Leveraging industrial funds with government (state and federal) funds from the Pennsylvania Ben Franklin Partnership Program
- Submitting joint proposals to such government programs as the National Institute of Standards and Technology's Advanced Technology Program and the Technology Reinvestment Program.

Licensing opportunities are also available for specific technologies.

Contacts:

The four principal investigators are:
Dr. Andrzej Badzian, Phone: (814) 865-1198
Dr. Russell Messier, Phone: (814) 865-3704
Dr. Rustum Roy, Phone: (814) 865-3421
Dr. Walter Yarbrough, Phone: (814) 865-7102

A general contact for IMRL is:
Ms. Vicki Zimmerman
The Pennsylvania State University
277 Materials Research Laboratory
University Park, PA 16802
Phone: (814) 865-3423
Fax: (814) 863-7039

Publications: For a complete list of the over 200 papers published by IMRL researchers, call one of the contacts listed above.

Research Triangle Institute

Description: The Research Triangle Institute, or RTI, (Research Triangle Park, NC) is involved in two efforts to achieve large-area, single-crystal, diamond heteroepitaxy. In the first effort, RTI is developing a technique known as tiling, in which an array of similarly oriented crystals are bonded to a non-diamond substrate. After doing so, a single-crystal diamond coating is deposited over the array. The second effort seeks to directly deposit a single-crystal coating over a large, non-diamond substrate.

<u>Tiling</u>
RTI's tiling process integrates several techniques to produce a single-crystal diamond sheet. In the first step of this process, RTI produces a homoepitaxial diamond crystal. To make this a sufficiently low-cost process, RTI has investigated several low-cost diamond CVD techniques, including a water-based process that, along with methanol, provides the required mix of carbon, hydrogen, and oxygen in the reaction chamber. RTI has found that the water-methanol mixture provides substantial savings in material costs and storage requirements without affecting the diamond growth rate or the technique's energy requirements.

After producing a homoepitaxial crystal, RTI removes a series of thin diamond sheets from the crystal. To do so, they use a technique known as ion implantation and lift-off, in which a beam of oxygen or carbon ions creates a buried, damaged layer within the diamond crystal. This damaged layer, whose depth can be precisely controlled as a function of the ion beam's energy, is turned to graphite after annealing the crystal. By preferentially etching the graphite from the crystal, researchers can then remove a thin diamond sheet from the crystal. Working with researchers at the University of North Carolina-Chapel Hill and Oak Ridge National Laboratory, RTI has demonstrated this technique on natural diamond crystals.

Once produced, these sheets can be bonded to a substrate to form an array of diamond tiles, all with the same crystalline orientation. Single-crystal diamond can then be deposited on this array. RTI is currently developing techniques to bond the thin diamond sheets to a non-diamond substrate and to grow diamond over this array.

As a part of this effort, RTI has also developed a series of advanced characterization techniques to count defect densities in diamond crystals, which is needed to find diamonds suitable for the lift-off method. These techniques, though, are also applicable to many other areas of diamond coating.

<u>Direct Deposition of Large-Area, Single-Crystal Diamond Coatings</u>
Due to the many obstacles to direct deposition, RTI is involved in several theoretical and experimental studies of this process. Some ongoing studies include:

- **Nickel Subsurface Studies**. Because nickel's lattice structure closely matches diamond's, it has been widely investigated as a possible substrate for diamond growth.

However, carbon-nickel bonds can be easily broken, and therefore diamond nucleation and growth on nickel is sporadic. In collaboration with North Carolina State University, RTI is investigating the energy effect of atoms embedded beneath the surface of the nickel lattice. The resulting model indicates that electropositive atomic species such as sodium may increase the bonding strength between a methyl radical and the nickel surface, while simultaneously stabilizing a diamond bonding configuration. By doing so, the electropositive species can open a path to diamond heteroepitaxy on nickel.

- **Molybdenum Interlayers on a Copper Substrate.** Like nickel, copper has a lattice structure that closely matches diamond's. Unfortunately, copper does not readily bond with carbon molecules, making it difficult to form a heteroepitaxial diamond layer on copper. To solve this problem, RTI has been investigating the possibility of alloying molybdenum, which forms strong carbon bonds, with the copper substrate. So far, this approach has yielded adherent diamond coatings; however, methods to improve the crystalline orientation of the diamond coating still need to be developed.

- **The Role of Oxygen.** RTI has pursued a series of studies to examine the role of oxygen in the diamond growth process. These studies indicate that oxygen can serve several roles. First, it can open sites for carbon to bond to the diamond lattice. Second, it can maintain or recover the diamond lattice structure by bonding to surface termination sites. Third, it can remove hydrogen from the surface (and thereby allow oxygen to carry out its other two roles). In addition, oxygen removes non-diamond carbon from the surface.

- **Local Carbon Sources.** By treating the substrate surface with various carbon-based molecules (such as sucrose, Teflon, and graphite), RTI has studied how these local sources of carbon can enhance the nucleation of diamond on a non-diamond substrate. RTI has found that longer carbon-chain species promote greater nucleation.

Opportunities for Collaboration: RTI already has a long history of collaboration with academic and industrial partners, both formally and informally, and is willing to consider similar collaborations on a case-by-case basis. In addition to the partnerships mentioned above, RTI has formed a joint venture with the 3M Company to refine an RTI-developed method for producing large-area diamond films. 3M provided financial and technical support to allow the recent construction of a manufacturing prototype-scale CVD reactor. The Advanced Research Projects Agency is also supporting commercialization of this work.

So far, RTI has applied for two patents related to its work in diamond, with other patent applications in progress.

Contacts:

Contacts for the overall project are:
Dr. Robert Markunus or Dr. Ron Rudder
Research Triangle Institute
3040 Cornwallis Road
P.O. Box 12194
Research Triangle Park, NC 27709-2194
Phone: (919) 541-6765
Fax: (919) 541-6515

For ion implantation and lift-off:
Dr. Max L. Swanson or Dr. Nalin Parikh
University of North Carolina, Chapel Hill
Department of Physics and Astronomy
Chapel Hill, NC 27599-3255
Phone (Parikh): (919) 962-7160
Phone (Swanson): (919) 962-0305

For nickel subsurface studies:
Dr. Jerry Whitten
North Carolina State University
School of Physical and Mathematical Sciences
Raleigh, NC 27694
Phone: (919) 515-7277

For characterization techniques:
Dr. Robert Nemanich
North Carolina State University
Department of Physics
Raleigh, NC 27695
Phone: (919) 515-3225

Publications: For a complete list of the over 70 papers published by RTI researchers and subcontractors, call Mrs. Gale Peed at (919) 541-5920.

Rice University

Description: A research group at Rice University (Houston, TX) is involved in several projects related to diamond thin-film production, including the development of new diamond CVD techniques:

- **Chlorine-Activated CVD** provides a less energetic chemical route to the production of atomic hydrogen. Because atomic hydrogen plays an important role in preventing the seed crystal from decomposing into graphite, more efficient production of atomic hydrogen results in higher growth rates at lower substrate and gas temperatures. These advantages are provided by the lower bond energy of dichlorine (60 kilocalories/mole) versus dihydrogen (101 kilocalories/mole) and by atomic chlorine's ability to chemically remove surface hydrogen at low temperatures. The Rice research group has demonstrated diamond growth rates greater than 5 microns per hour at 850°C, 0.3 microns per hour at 250°C, and measurable growth at 100°C.

- **Fluorocarbon Pyrolysis CVD** takes advantage of elemental fluorine's ability to react with graphite but not with diamond. The technique uses an alternating growth/etch cycle. In the growth stage, fluorocarbon molecules chemically decompose into carbon tetrafluoride and carbon when heated (thus the term fluorocarbon pyrolysis), with carbon depositing as diamond at appropriate substrate temperatures. In the etch stage, elemental fluorine etches graphitic carbon only, leaving diamond. This research is expected to result in a hydrogen-free method for diamond CVD.

- **Laser Plasma CVD** takes advantage of focused laser light to make gas molecules and micron-sized particles decompose in a locally contained plasma. By doing so, a laser can optimize plasma production over very small areas. The method is particularly suited to deposition of strongly bonded diamond composites. The Rice research group is evaluating various conditions and gas/solid mixtures to adapt the process to different needs.

Rice is also developing *in situ* diagnostics for diamond CVD and investigating methods to anneal diamond surfaces using ultraviolet pulsed lasers. As part of the first effort, the Rice researchers have developed a laser interferometric growth monitor that can measure diamond growth *in situ* with an accuracy of about 5 nanometers. In the second effort, they hope to reduce the strain and defect content in diamond during growth by heating the area near the substrate surface to high temperatures. This heating occurs by directing ultraviolet laser beams with nanosecond and picosecond pulse widths at the surface.

Opportunities for Collaboration: The chlorine-activated and fluorocarbon diamond CVD growth processes have been patented or are in the patent-pending stage by the Houston Advanced Research Center. These patents are available for license.

In other areas of research, opportunities for collaboration are currently limited to information transfer. However, future opportunities will likely develop as the research progresses.

Contacts:

Technical contact:
Dr. Robert H. Hauge
Rice University
Department of Chemistry
P.O. Box 1892
Houston, TX 77251
Phone: (713) 527-4082
Fax: (713) 285-5155

Licensing information:
Kerri Smith
Houston Advanced Research Center
4800 Research Forest Drive
The Woodlands, TX 77381
Phone: (713) 363-7934
Fax: (713) 363-7935

Publications:

Patterson, E. Don et al. "Halogen-Assisted Deposition of Diamond," *U.S. Patent No. 5,071,677*, December 10, 1991.

Chu, C. Judith, et al. "Mechanism of Diamond Film Growth by Hot-Filament CVD: Carbon-13 Studies," *Journal of Materials Research*, Vol. 5, No. 11, November 1990.

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SI Diamond Technology, Inc.

Description: With the help of BMDO SBIR contracts and a licensing agreement with the University of Texas at Dallas, SI Diamond Technology, Inc. (Houston, TX) has become a leader in diamond coating technology. The company is pursuing both near-term commercialization of diamond thin film technology and R&D projects with longer term benefits.

SI Diamond's current commercialization efforts largely involve Amorphic Diamond™, a patented diamond-like coating developed at the University of Texas at Dallas, or UTD (see page 48). Amorphic Diamond™ coatings (ADCs) are produced using a laser ablation process. Because the substrate remains at a relatively low temperature during the process (about 35°C), ADCs can be grown on almost any substrate. ADCs also emit electrons at much lower power levels than other materials, making them an attractive cold cathode. Unlike virtually any other cathode, ADCs are not easily poisoned by exposure to air, water, and other environments. As a result , field-emission displays (whose traditional strength has been ease-of-manufacture) made with ADC-based cathodes could produce images of equal or better quality than active-matrix liquid crystal displays.

SI Diamond's R&D projects have two primary thrusts: One is to deposit single-crystal diamond on non-diamond substrates and the other is to develop doping processes to make diamond semiconductors. In the area of single-crystal deposition, SI Diamond's current emphasis is on atomic layer epitaxy (ALE), although the company is also pursuing other techniques such as seeded supersonic beams. The company has also developed and patented a fast atom doping process and is now testing possible dopants to make n- and p-type semiconductors. Development of these two processes will be needed before any company can fully exploit diamond's famed properties for electronics applications.

As part of the BMDO Diamond Technology Initiative, SI Diamond has received 14 BMDO SBIR contracts: Four have received Phase II funding, three have received Phase I funding only, and seven only recently began in the past year. The Phase II projects include:

- **Atomic Layer Epitaxy.** In a BMDO SBIR project, SI Diamond is developing an ALE process aimed at depositing single-crystal diamond on a non-diamond substrate. Through self-limiting chemical reactions at the substrate surface, ALE can provide better-controlled growth than CVD techniques, thereby ensuring that growth occurs one atom-thick layer at a time.

- **Fast Atom Doping.** In another BMDO SBIR project, SI Diamond developed a fast atom doping (FAD) process in which researchers shoot atoms at a diamond film during CVD growth. By doing so, the process adds the impurities necessary for the eventual manufacture of n-type semiconducting diamond. To date, no other technology can reliably dope diamond films without damaging the natural crystalline structure of the film. SI Diamond is currently testing a variety of dopants to make both n- and p-type semiconductors.

- **Nucleation and Growth of Epitaxial Diamond.** In the Phase I program, SI Diamond demonstrated the first direct probe for diamond surface chemistry under a low-pressure chemical vapor deposition process: in-situ direct recoil spectroscopy (DRS). In the Phase II program, SI Diamond is using this information to establish a process to deposit single-crystal diamond on a non-diamond substrate.

- **Seeded Supersonic Beam Deposition of Diamond.** In this technique, collisions between gas feedstock molecules and the substrate provide the activation energies needed to produce diamond coatings. The supersonic expansion of a lighter carrier gas provides the necessary acceleration; this expansion can provide a precisely controlled kinetic energy, thereby allowing well-controlled, epitaxial growth.

SI Diamond also recently began research to:

- Use cubic boron nitride coatings in industrial and electronic applications
- Deposit large-area, single crystal diamonds
- Develop a laser-based diamond growth process
- Develop diamond-metal interconnects to facilitate heat removal from multi-chip modules
- Increase the current density of high power amplifiers and pulsed energy sources using diamond cold cathodes
- Investigate the use of ion beam technology to directly write interconnect wires on multi-chip modules.

Opportunities for Collaboration: SI Diamond recently became the first diamond coating start-up to become publicly owned when it completed an initial public offering of nearly $5 million in stock in 1993. Also, in 1994 SI Diamond opened a commercial ADC coating facility and offers diamond coating services for original equipment manufacturers that wish to out-source their coating requirements. Niche markets that the company plans to pursue include diamond-coated surgical tools, dental instruments, mechanical bearings, electronic components, and other small, high-value items. In addition, SI Diamond has also been extremely active in collaborating with, and licensing technology from, other organizations. Its largest effort, however, is focused on commercializing an ADC-based field-emission display. In June of 1994, SI Diamond announced that it had developed what is probably the world's first working prototype of a diamond-based field emission display.

<u>Patents and Licensing Agreements:</u>
SI Diamond has licensed exclusive worldwide rights to manufacture and sell equipment and services related to laser ablation of ADCs from UTD. The licensing agreement also includes rights to sublicense the process. In addition to the ADC license, SI Diamond has received a patent for its fast atom doping process and has a patent pending for its chemically-catalyzed diamond-growth technology.

SI Diamond has also licensed a laser-based growth method from McDonnell-Douglas Corporation and will use the technology in one of the company's current SBIR projects.

Ventures

SI Diamond has entered several ventures aimed to spur development of flat-panel-displays that use diamond cold-cathodes, the first of which is a joint technology demonstration project with the Microelectronics and Computer Technology Corporation (MCC). In this project, SI Diamond and the consortium of computer companies will cross-license and pool all technologies pertinent to these diamond-based, field-emitter displays. SI Diamond expects to begin manufacturing flat-panel displays in limited quantities in manufacturing facilities leased from MCC as early as the middle of 1994. In other flat-panel display ventures, SI Diamond has:

- Teamed with the David Sarnoff Research Center to perfect color phosphors and screens for the flat-panel displays

- Agreed with Fischer Imaging Corporation (Denver, CO) to co-develop a flat-panel display system for digital mammography

- Acquired Plasmatron Coatings and Systems, Inc. (Cinnaminison, NJ), a designer and builder of coating and vacuum systems.

In addition, SI Diamond has signed a cooperative research and development agreement with Lawrence Livermore National Laboratory (LLNL) to determine, along with Commonwealth Scientific (Alexandria, VA), whether LLNL's cathodic arc deposition technique could be used in the production of novel, advanced hard coatings. SI Diamond has also teamed with Wayne State University, Ohio University, and the University of California at Los Angeles in two of the company's current SBIR projects.

Other Commercialization Efforts

SI Diamond is in the process of building an Amorphic Diamond™ coating facility, which will allow the company to begin commercial coating programs. Further in the future, SI Diamond hopes to offer a line of diamond-coating equipment suitable for many industries.

Contacts:

Dr. Howard Schmidt, Chief Scientist and COO
Dr. Mark Hammond, Investigator
Ms. Marijane Ensminger, Director of Investor Relations
SI Diamond Technology, Inc.
2435 North Boulevard
Houston, TX 77098
Phone: (713) 529-9040
Fax: (713) 529-1147

Technology Assessment & Transfer, Inc.

Description: Technology Assessment & Transfer, Inc., or TA&T (Annapolis, MD), produces diamond coatings using an oxy-acetylene torch. This method allows TA&T to produce coatings that compare in quality to CVD processes, but with several important cost advantages. First, the oxy-acetylene torch is faster; it can produce diamond thin-films at a growth rate of about 50 microns per hour, compared to about 1 micron per hour for most CVD processes. The faster growth rate is essential for mass production of diamond-coated products, since the highly-skilled labor needed to produce diamond coatings imposes the highest cost in any large-scale production environment. Second, the oxy-acetylene torch can deposit films at atmospheric pressure, thereby eliminating the need for the expensive vacuum chambers found in CVD reactors. As a result, inserts can be coated continuously, rather than in batches. Due to its simplicity, the oxy-acetylene torch also provides users with a low capital investment, low operating costs, and reduced maintenance requirements.

However, before the oxy-acetylene technique can move to the production floor, better process control techniques need to be developed to make the technique more repeatable. For example, TA&T is investigating the purity of the acetylene tanks, where small amounts of acetone can adversely affect the quality of the diamond coating. TA&T also hopes to develop methods to more precisely control other key parameters—such as temperature, flow rate, and the shape of the flame—through computer numerical control techniques.

In a project funded by the BMDO Technology Applications Office, TA&T worked to produce diamond-coated cutting tools using their oxy-acetylene torch. TA&T has also used their technique to produce diamond-coated infrared windows and diamond heat spreaders for integrated circuits.

Opportunities for Collaboration: TA&T has entered into a cooperative research and development agreement with the Naval Research Laboratory's Optical Sciences Division to develop diamond coatings for infrared windows. The company is also interested in building a scalable research facility that would allow TA&T to train others in depositing diamond coatings with an oxy-acetylene torch. The company believes that their process control technology, when further developed, will provide a good licensing opportunity for companies working with diamond coatings.

Contact:
Dr. David Palaith
133 Defense Highway, Suite 212
Annapolis, MD 21401
Phone: (410) 224-3710
Fax: (410) 224-4678

ThermoTrex Corporation

Description: Because it is difficult to reliably dope diamond semiconductors, only a few, simple active diamond electronic devices—such as diodes and field emitters—are regularly made in the laboratory. ThermoTrex Corporation (San Diego, CA), however, is developing three-terminal diamond electronic devices that use an electron-beam as the third terminal. By bombarding a diamond insulator with electrons, the electron beam creates carrier pairs in the diamond and temporarily turns the diamond into a conductor.

As in traditional transistors, this electron-beam activated switching produces a current gain. So far, these switches have demonstrated gains from 500x to 2,000x, depending on the input current and voltage levels. By modulating the electron-beam, the resulting conductivity of the diamond switch is also modulated. As a result, this technology can be used as a microwave power source at high frequencies.

So far, ThermoTrex has built working diamond switches and millimeter wave amplifiers. The frequency range of these devices spans from under 1 megahertz to 35 gigahertz. At 1 gigahertz, power levels of 16 kilowatts have been demonstrated, while higher power levels should be possible. Although ThermoTrex has used natural diamond to make these devices, the company also plans to develop similar devices using CVD diamond.

Opportunities for Collaboration: ThermoTrex researchers anticipate that a fully developed prototype is still 1 to 2 years away; however, early results indicate that their electron-beam activated devices can work at very high power levels, providing useful devices at microwave and millimeter wave frequencies. ThermoTrex will consider collaborations with any party interested in helping to produce marketable devices. Possible applications identified to date include efficient, high-repetition-rate, high-power switching; advanced accelerators; millimeter wave missile seeker systems; and high-power broadcast and radar transmitter systems. ThermoTrex has been granted three patents for the electron-beam activated diamond transistors, one of which is held in collaboration with Varian Associates.

Contact:
Dr. Shiow-Hwa Lin
ThermoTrex Corporation
9550 Distribution Ave.
San Diego, CA 92121-2306
Phone: (619) 578-5885/536-8420
Fax: (619) 578-1419

Publications:
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University of Texas at Dallas

Description: The Center for Quantum Electronics at the University of Texas at Dallas (UTD) has developed a laser ablation process for producing diamond thin films from a graphite feedstock. This development is the result of gamma ray laser research funded by the BMDO Innovative Science and Technology program. In this process, a pulsed laser heats the graphite feedstock in a low pressure, ultrahigh vacuum system. By heating the graphite, the laser creates a plasma vapor that contains energetic carbon ions. When the carbon ions settle on a substrate, they produce nanophase (materials composed of nanometer-sized particles of a single phase) diamond films called Amorphic Diamond™. Because the substrate remains at a relatively low temperature during the process (about 35° C), Amorphic Diamond™ can be grown on almost any substrate—including silicon, titanium, gold, silver, aluminum, copper, stainless steel, ceramics, and polyimide—at a rate of 0.5 microns/hr over a 100 cm^2 area.

Unlike other diamond-like films, Amorphic Diamond™ contains almost no hydrogen atoms, whose presence can vary the properties of a diamond film and cause it to break down in extreme conditions such as high temperature or radiation. Amorphic Diamond™ consists of densely packed nodules of diamond crystals linked by a network of other carbons. The better the packing, the closer Amorphic Diamond™'s mechanical properties approach those of natural crystalline diamond.

Nodule packing density is directly related to how much the laser heats the carbon plasma. To increase packing density, the UTD research team has developed a planetary drive system that rotates the substrate so that only ions energetic enough for close packing are deposited on the surface. As a result, Amorphic Diamond™ coatings can have a diamond content as high as 85 percent and hardness nearly equal to or possibly better than natural diamond. Furthermore, Amorphic Diamond™ coatings are less brittle than crystalline diamond, and bond better to the substrate because they have less internal stress. Low internal stress also allows the UTD process to deposit films up to 5 microns thick.

Amorphic Diamond™ is best suited to applications in wear protection, where one to three micron-thick films can extend the lifetime of materials against the erosive effects of high-speed particles and droplets up to a thousand-fold. One advantage of Amorphic Diamond™ over other synthetic diamonds is that the laser ablation process forms a natural interlayer between the substrate and the coating, thereby resulting in strong adhesion.

In addition, Amorphic Diamond™ is a natural n-type semiconductor, making the material suitable for some microelectronics applications, such as diamond cold cathodes. However, Amorphic Diamond™ cannot provide the single-crystal coating required for most microelectronics applications.

Opportunities for Collaboration: The University of Texas at Dallas has received two U.S. patents for the laser ablation technology, with several more pending. With several European patents issued, UTD also has received extensive international patent coverage. They have

licensed exclusive rights to manufacture and sell equipment for the laser ablation process to SI Diamond Technology, Inc. (Houston, TX). SI Diamond also has licensed rights for optical applications of the technology (see page 42).

Further, UTD received a grant from the State of Texas to help companies evaluate Amorphic Diamond™ coatings on a wide variety of products. UTD invites interested companies to have UTD coat a product of theirs with Amorphic Diamond™. Once coated, the companies can evaluate the product on their own before considering a licensing arrangement or other venture.

Some of the products UTD has coated to date include:

- **Optical windows, lenses, and mirrors.** Zinc sulfide infrared windows coated with a 2.5 micron-thick coating of Amorphic Diamond™ have passed a wide range of erosion tests. The coating also can be used in x-ray optics.

- **Machine tool and surgical instrument coatings.** Amorphic Diamond™ has the versatility to adhere to almost any material and increase its wear lifetime.

- **Computer disk coatings.** To increase packing densities, computer-makers must move the head closer to the hard disk. Unfortunately, closer contact between the computer head and the disk causes more bit errors. Amorphic Diamond™ coatings prevent these errors; as a result, disks with Amorphic Diamond™ coatings could store megabytes more information than now possible.

- **Medical implant coatings.** Amorphic Diamond™'s compatibility with human tissue makes it an ideal coating for titanium and stainless steel implants used for bone replacements or cardiac pacemakers.

Contact:
Dr. Carl Collins
University of Texas at Dallas
Center for Quantum Electronics
P.O. Box 830688
Richardson, TX 75083-0688
Phone: (214) 690-2864
Fax: (214) 690-1167

Publications:
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Wayne State University

Description: Wayne State University is currently in the second year of a 3-year, BMDO-sponsored program to deposit heteroepitaxial diamond on silicon. A major barrier to this goal is the lattice mismatch between diamond and silicon, resulting in epitaxial stresses between the silicon surface and diamond films. To reduce these lattice strains, Wayne State researchers first grow an interlayer of cubic boron nitride (c-BN) on the silicon surface. After doing so, they grow a thin precursor layer of diamond on the c-BN surface. Diamond's lattice structure closely matches that of c-BN, thereby relieving the lattice stresses that prevent single-crystal growth.

To deposit both the c-BN and precursor diamond films, the researchers use a reactive laser ablation system. This system includes a capacitive power supply that dumps extra energy near the substrate, thereby allowing for precisely controlled growth as in conventional CVD systems. After depositing the precursor diamond, conventional CVD processes can be used to grow single-crystal diamond films on the crystal.

The researchers have successfully deposited the c-BN interlayer using this system and have achieved some promising results in initial experiments with diamond. In their experiments, the Wayne State researchers have found sparsely nucleated diamond on the c-BN surface, along with small areas of single-crystal orientation. The researchers characterized the diamond film using thermal characterization techniques, channeling analysis, and Fourier transform infrared spectroscopy. Efforts are now underway to increase the nucleation density of the precursor diamond and produce single-crystal growth over a large area.

Opportunities for Collaboration: Wayne State is currently collaborating with SI Diamond Technology, Inc. in two BMDO SBIR programs, one involving the deposition of c-BN and another involving heteroepitaxial diamond growth on silicon. The university is interested in transferring the results of its research to industry, and will consider collaborations like that with SI Diamond on a case-by-case basis.

So far, six diamond-related patents have been issued to Wayne State University, three of which are related to Wayne State's work for BMDO.

Contact:
Dr. Roger W. Pryor
Wayne State University
666 W. Hancock St.
Detroit, MI 40821
Phone: (313) 577-0846
Fax: (313) 577-7743

Publications: Three journal articles related to this work are currently in press. To receive copies when they are completed, please contact Dr. Pryor.

West Virginia University

Description: Researchers at West Virginia University, or WVU (Morgantown, WV), are developing a new nucleation and growth technique known as catalyzed diamond epitaxy (CDE). By eliminating some of the process limitations of conventional deposition techniques (such as long induction periods, low growth rates, and the inefficient use of hydrogen), this technique may allow researchers to grow heteroepitaxial layers of electronic-grade, single-crystal diamond.

This technique is based on ultrahigh vacuum (UHV) CVD technology, an approach that has never before been investigated for depositing diamond thin films. Comparable to gas source MBE and related techniques, UHV CVD technology will, if successful, allow the growth of diamond under well-controlled conditions; in addition, it will allow *in situ* characterization of the nucleation and growth process.

CDE uses a surface catalyst, such as silicon, to stabilize the diamond surface structure and generate vacant surface sites. In conventional processes, this role is played by hydrogen. However, when hydrogen bonds to the diamond surface to stabilize the diamond structure, it produces a relatively inert surface. This chemical stability makes it difficult for the next step, hydrogen abstraction, to open a bonding site for carbon species. The low probability of hydrogen abstraction leads to slow growth rates, inefficient use of hydrogen, and polycrystalline growth.

Work on this process has also led WVU researchers to investigate other aspects of diamond nucleation and growth. First, they are investigating the surface conditions required for heteroepitaxial nucleation. The first part of this research involves finding the conditions under which the substrate surface will be converted to carbon-rich molecular species. The second part involves finding the conditions under which diamond will nucleate on or in these carbon-rich species.

The WVU researchers have also found that molecular hydrocarbon species were not sufficiently reactive to provide the desired growth rates for CDE. As a result, they are developing a well controlled, selective, UHV-compatible CH_x radical source to replace molecular hydrocarbon species as a gaseous precursor.

Even if this work does not led to a technique for depositing electronic-grade diamond, the research should still provide mechanistic information that could be used to optimize existing processes. Furthermore, the WVU researchers are investigating CDE as a method for producing wide bandgap materials such as gallium nitride. So far, the technique has been used to produce high-quality thin films and heterostructures of materials such as silicon and silicon/germanium.

Opportunities for Collaboration: As a relatively new research program, opportunities for collaboration are currently limited to information transfer; however, since the goal of this research is to develop a marketable deposition process or materials, future opportunities are likely to develop.

Contact:
Dr. Charter D. Stinespring
Department of Chemical Engineering
West Virginia University
P.O. Box 6101
Morgantown, WV 26506-6101
Phone: (304) 293-2111
Fax: (304) 293-5024

Publications: As a new research program, all publications are still in press. In the meantime, please contact Dr. Stinespring for more information.

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